CLAIMS

We Claim:

1. A catalyst system comprising a bulky ligand hafnium transition metal metallocene-type catalyst compound, wherein at least one bulky ligand is substituted with a substituent having 3 or more non-hydrogen atoms.

2. The catalyst system in accordance with claim 1 wherein the at least one bulky ligand is substituted with a substituent having 3 or more carbon atoms.

3. The catalyst system in accordance with claim 1 wherein the at least one bulky ligand is substituted with at least one alkyl having 3 or more carbon atoms.

4. The catalyst system in accordance with claim 1 wherein the catalyst compounds comprises two bulky ligands.

5. The catalyst system in accordance with claim 4 wherein at least one bulky ligand is a cyclopentadienyl derived ligand that is substituted with at least one alkyl having 3 or more carbon atoms.

6. The catalyst system in accordance with claim 1 wherein the substituent is selected from one or more of the group consisting of n-propyl, isopropyl, n-butyl, isobutyl and n-pentyl.

7. The catalyst system in accordance with claim 1 wherein the at least one bulky ligand is substituted with at least 3 or more non-hydrogen atoms one of which is a silicon atom.

8. The catalyst system in accordance with claim 1 wherein the bulky ligand hafnium transition metal metallocene-type catalyst compound is represented by the formula:

$$(C_5H_{5-d-f}R''_d)_eR'''_fHfQ_{g-e}$$

wherein ($C_5H_{5-d-f}R"_d$) is an unsubstituted or substituted cyclopentadienyl ligand bonded to Hf, wherein at least one ($C_5H_{5-d-f}R"_d$) is substituted with at least one R" is an alkyl substituent having 3 or more carbon atoms, each additional R", which can be the same or different is hydrogen or a substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, R"' is one or more or a combination of the group consisting of carbon, germanium, silicon, phosphorous and nitrogen atoms containing radical bridging two ($C_5H_{5-d-f}R"_d$) rings, or bridging one ($C_5H_{5-d-f}R"_d$) ring to Hf; each Q which can be the same or different is selected from the group consisting of a hydride, substituted and unsubstituted hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides and combination thereof ; two Q's together form an alkylidene ligand or cyclometallated hydrocarbyl ligand or other divalent anionic chelating ligand; where g is an integer corresponding to the formal oxidation state of Hf, d is 0, 1, 2, 3, 4 or 5, f is 0 or 1 and e is 1, 2 or 3

9. The catalyst system of claim 8 wherein d is 1, 2, 3 or 4, e is 2 and f is O.

10. A process for polymerizing olefin(s) in the presence of a catalyst system comprising a bulky ligand hafnium transition metal metallocene-type catalyst compound having at least one bulky ligand substituted with a substituent having 3 or more non-hydrogen atom, and an activator.

11. The process in accordance with claim 10 wherein the substituent has 3 or more carbon atoms.

12. The process in accordance with claim 10 wherein the bulky ligand is one or more cyclopentadienyl derived ligands, wherein one of the cyclopentadienyl derived ligands is substituted with at least one alkyl having 3 or more carbon atoms.

13. The process in accordance with claim 12 wherein the bulky ligands are two cyclopentadienyl derived ligands each substituted with at least one alkyl substituent having 3 or more carbon atoms.

14. The process in accordance with claim 10 wherein the substituent is selected from one or more of the group consisting of n-propyl, isopropyl, n-butyl, isobutyl and n-pentyl.

15. The process in accordance with claim 10 wherein at least one bulky ligand is substituted with at least 3 or more non-hydrogen atoms one of which is a silicon atom.

16. The process in accordance with claim 10 wherein the olefin(s) are alpha-olefins having from 2 to 12 carbon atoms.

17. The process in accordance with claim 10 wherein the olefin(s) are ethylene in combination with one or more other alpha-olefins having from 3 to 10 carbon atoms.

18. The process in accordance with claim 10 wherein the process is a gas phase process.

19. The process in accordance with claim 10 wherein the catalyst system further comprises a support.

20. The process in accordance with claim 10 wherein the bulky ligand hafnium transition metal metallocene-type catalyst compound is bis(n-propyl-cyclopentadienyl) hafnium dichloride.

21. A continuous gas phase process for polymerizing olefin(s) in a fluidized bed gas phase reactor in the presence of a catalyst system to produce a polymer product, the catalyst system comprising a bulky ligand hafnium transition metal metallocene-type catalyst compound having at least one bulky ligand substituted with a substituent having 3 or more carbon atoms, and the polymer product comprising less than 2 ppm hafnium.

12 11
~~22~~. The process of claim ~~21~~ wherein the polymer product comprises less than 1 ppm hafnium.

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~~23~~. The process in accordance with claim ~~21~~ wherein the catalyst system is supported.

24. The process in accordance with claim 21 wherein the substituent is an alkyl having 3 to 10 carbon atoms.

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~~25~~. The process in accordance with claim ~~21~~ wherein the polymer product has a density greater than 0.915 g/cc.

26. The process in accordance with claim 21 wherein the olefin(s) are ethylene and at least one alpha-olefin having 3 to 8 carbon atoms.

27. The process in accordance with claim 21 wherein the catalyst system is represented by the formula:

$$(C_5H_{5-d-f}R''_d)_eR'''_fHfQ_{g-e}$$

wherein $(C_5H_{5-d-f}R''_d)$ is an unsubstituted or substituted cyclopentadienyl ligand bonded to Hf, wherein at least one $(C_5H_{5-d-f}R''_d)$ is substituted with at least one R" is an alkyl substituent having 3 or more carbon atoms, each additional R", which can be the same or different is hydrogen or a substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, R''' is one or more or a combination of the group consisting of carbon, germanium, silicon, phosphorous and nitrogen atoms containing radical bridging two $(C_5H_{5-d-f}R''_d)$ rings, or bridging one $(C_5H_{5-d-f}R''_d)$ ring to Hf; each Q which can be the same or different is selected from the group consisting of a hydride, substituted and unsubstituted hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides and combination thereof ; two Q's together form an alkylidene ligand or cyclometallated hydrocarbyl ligand or other divalent anionic chelating ligand; where g is an integer

corresponding to the formal oxidation state of Hf, d is 0, 1, 2, 3, 4 or 5, f is 0 and e is 1, 2 or 3, and the polymer product has a melt index less than 0.1 dg/min without the addition of hydrogen to the process.

28. A continuous slurry phase process for polymerizing olefin(s) in the presence of a catalyst system to produce a polymer product in a liquid polymerization medium, the catalyst system comprising a bulky ligand hafnium transition metal metallocene-type catalyst compound having at least one bulky ligand substituted with a substituent having 3 or more carbon atoms, and the polymer product comprising less than 2 ppm hafnium.

29. The process in accordance with claim 28 wherein the polymer product comprises less than 1 ppm hafnium.

30. The process in accordance with claim 28 wherein the density is greater than 0.900 g/cc.

31. The process in accordance with claim 28 wherein the olefins are ethylene and at least one alpha-olefin having 3 to 8 carbon atoms.

32. The process in accordance with claim 28 wherein the catalyst system is represented by the formula:

$$(C_5H_{5-d-f}R''_d)_eR'''_fHfQ_{g-e}$$

wherein $(C_5H_{5-d-f}R''_d)$ is an unsubstituted or substituted cyclopentadienyl ligand bonded to Hf, wherein at least one $(C_5H_{5-d-f}R''_d)$ is substituted with at least one R" which is an alkyl substituent having 3 to 10 carbon atoms, each additional R", which can be the same or different is hydrogen or a substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, R''' is one or more or a combination of the group consisting of carbon, germanium, silicon, phosphorous and nitrogen atoms containing radical bridging two $(C_5H_{5-d-f}R''_d)$ rings, or bridging one $(C_5H_{5-d-f}R''_d)$ ring to Hf; each Q which can be the same or different is

sélected from the group consisting of a hydride, substituted and unsubstituted hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides and combination thereof ; two Q's together form an alkylidene ligand or cyclometallated hydrocarbyl ligand or other divalent anionic chelating ligand; where g is an integer corresponding to the formal oxidation state of Hf, d is 0, 1, 2, 3, 4 or 5, f is 0 or 1 and e is 1, 2 or 3, and the polymer product has a melt index less than 0.1 dg/min without the addition of hydrogen to the process.

33. A polymer produced with a hafnocene catalyst system, the polymer comprising ethylene and having a hafnium content in the range of 0.1 to 1 ppm.

34. The polymer in accordance with claim 33 wherein the polymer further comprises an alpha-olefin having from 3 to 10 carbon atoms.

35. The polymer in accordance with claim 33 wherein the polymer has a density greater than 0.915 g/cc.

36. A polyethylene polymer produced with a hafnocene catalyst system, the polymer having a density in the range of 0.865 to 0.97 g/cc, a Mw/Mn in the range of between 2 to 3 and a hafnium content of less than 2 ppm.

37. The polymer in accordance with claim 36 wherein the polymer has a hafnium content less than 1 ppm.

38. The polymer in accordance with claim 36 wherein the polymer has a melt index less than 3 dg/min.

39. The polymer in accordance with claim 36 wherein the polymer has a settled bulk density in the range of 15 to 30 lb/ft^3 (240 to 481 kg/m^3).

40. The polymer in accordance with claim 36 wherein the polymer is a homopolyethylene having a density greater than 0.950 g/cc.

41. The polymer in accordance with claim 36 wherein the polymer contains a support material selected from the group consisting of silica, alumina, and magnesium.

42. The polymer in accordance with claim 36 wherein the hafnocene catalyst system contains a mole ratio of aluminum to hafnium in the range of 50:1 to 500:1.

43. The polymer in accordance with claim 36 wherein the polymer has in the range of between 0.03 to 100 ppm aluminum.

44. The polymer in accordance with claim 36 wherein the hafnocene catalyst system is unbridged.

45. An ethylene based polymer produced by a catalyst system comprising a bulky ligand hafnium transition metal metallocene-type catalyst compound, wherein at least one bulky ligand is substituted with a substituent having 3 to 5 carbon atoms, the polymer having a settled bulk density in the range from 15 to 30 lb/ft^3 (240 to 481 kg/m^3), a Mw/Mn in the range of from 2 to 3, a density in the range of from 0.900 g/cc to greater than 0.97 g/cc and a hafnium content in the range of from 0.1 to 1 ppm.

46. The polymer in accordance with claim 45 wherein the polymer has a density greater than 0.915 g/cc and a melt index less than 1 dg/min.

47. The polymer in accordance with claim 45 wherein the polymer is selected from the group consisting of an ethylene/butene-1 copolymer, an ethylene/4-methyl-1-pentene copolymer, an ethylene/hexene-1 copolymer and an ethylene/octene-1 copolymer.

48. The polymer in accordance with claim 45 wherein the substituent is a linear alkyl.

49. The polymer in accordance with claim 45 wherein the polymer comprises a support material.

50. The polymer in accordance with claim 45 wherein the polymer contains in the range of from 0.03 to 100 ppm aluminum.

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